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(54) Title: CERAMIC PRODUCT BASED ON LITHIUM ALUMINIUM SILICATE (57) Abstract A ceramic product, particularly one for handling molten aluminium, which contains at least 70 % lithium aluminium silicate on a mass per mass basis is disclosed as well as a method of improving the non-wettability of the product.		

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CERAMIC PRODUCT BASED ON LITHIUM ALUMINIUM SILICATE

Technical Field

This invention relates to a ceramic product, and then particularly one for
5 handling molten aluminium.

In this specification the term 'ceramic product' refers to a product which has
been formed by firing a ceramic raw material to a suitable temperature.

10

Background Art

Molten aluminium, which has a relatively low melting point of $\pm 700^{\circ}\text{C}$, is
difficult to handle and for this reason the apparatus used usually comprises a
product that has a high thermal shock resistance, a high resistance to
15 wettability, a low thermal conductivity/capacity, and high strength.

None of the products which has hitherto been used for the aforesaid purpose,
amongst others aluminium titanate; fused silica; cast iron and fibrous ceramic
board, has ideal properties in this regard.

20

Object of the invention

It is an object of this invention to provide a ceramic product which the applicant
believes has advantages over the known arrangements.

Disclosure of the invention

According to the invention a ceramic product is provided which contains at least 70% lithium aluminium silicate on a mass per mass basis.

5

Lithium aluminium silicate (hereafter referred to as LAS) occurs naturally as the mineral petalite, and is used in small quantities in ceramic formulations instead of feldspar in order to decrease the thermal expansion of such formulations, and hence improve their resistance to thermal shock. It is also used in glass compositions for stove tops and oven ware.

10

Applicant has now found that an LAS-ceramic product according to the invention has extremely low thermal expansion and can hence as such be used in any apparatus subjected to any form of heat exposure, such as for example, that occurring in the handling of molten aluminium.

15

Such an LAS-ceramic product can be manufactured by forming a suitable quantity of finely divided petalite in any of the conventional methods such as slip casting; extrusion or injection moulding; and wet or dry pressing and then firing it at a temperature in the order of between 1150°C and 1210°C.

20

For use in the aluminium industry, such an LAS-ceramic product does not have to be fired to full density. It has been found that fired densities of the order of

60 to 70% of the theoretical are obtained when firing at between 1150 and 1210°C. At these densities, the product shows no dimensional changes, no thermal expansion, adequate strength (MoR 30 to 40 MPa), a low thermal conductivity and thermal capacity, and also takes an excellent coating when
5 painted with protective materials such as boron nitride, as is normal practice in the aluminium industry. It can furthermore be impregnated with liquid substances intended for enhancing the metallurgical properties of the product.

If required, the density of the LAS-ceramic product can be lowered by the
10 addition of fly ash microspheres and/or a suitable combustible material.

Further according to the invention the LAS-ceramic product according to the invention includes a non-wetting agent which has been incorporated in the fired LAS-ceramic product.

15

The reason for such incorporation is that the inherent wettability of LAS by molten aluminium poses severe problems when the protective coating usually provided on the LAS-ceramic product is removed, which may, for example, happen during use of the ceramic product.

20

It has furthermore been found that such wettability cannot be reduced by the incorporation of known non-wetting agents in the ceramic formulation of the product according to the invention, because such agents tend to react with the

LAS during the firing process causing them to lose their ability as non-wetting agents.

Furthermore, by incorporating the non-wetting agent in the fired LAS-ceramic product, the thermal expansion properties of the ceramic product are not adversely affected.

Further according to the invention the non-wetting agent comprises barium sulphate (BaSO_4), which is a well known non-wetting agent in the ceramic industry.

Further according to the invention a method for improving the non-wettability of an LAS-ceramic product is provided which includes the step of providing a suitable non-wetting agent such as BaSO_4 in the fired LAS-ceramic product.

In one form of the invention the BaSO_4 may be provided in the fired LAS-ceramic product by impregnating the semi-porous fired LAS-ceramic product with a saturated aqueous solution of barium sulphide (BaS) which, after drying, is oxidised in situ to BaSO_4 .

Such oxidation may be effected by calcining the dried product to 500 - 800°C in an oxidising atmosphere.

Commercial BaS can be used, or BaS can be prepared by the reduction of BaSO_4 with carbon at 1190°C , or with ammonia at 1000°C .

In another form of the invention the BaSO_4 may be provided by impregnating
5 the semi-porous fired LAS-ceramic product with a solution of BaCl_2 , and then treating the product with sulphuric acid to cause BaSO_4 to precipitate inside the pores of the ceramic product.

Preferably the BaCl_2 -solution is a substantially saturated one, and the sulphuric
10 acid comprises diluted sulphuric acid.

The BaCl_2 - solution can either be prepared by dissolving BaCl_2 in water, or by treating BaCO_3 with hydrochloric acid.

15 In a preferred form of the invention the ceramic product according to the invention comprises substantially 100% LAS (mass per mass).

Best mode for carrying out the invention

A semi-porous LAS-ceramic product according to the invention comprising
20 100% (mass per mass) LAS is provided by forming a suitable quantity of petalite in finely divided form by means of any one of the conventional methods such as slip casting; extrusion of injection moulding; or wet or dry pressing, and firing the formed product at a temperature of between 1150°C and 1210°C .

Preferably said finely divided petalite comprises a mixture of two fractions :

- a first one having an average particle size in the order of 1 micrometer, used in a concentration from 50 to 100% (mass per mass); and
- 5 - a second one having a particle size finer than 75 micrometer, used in a concentration of from 0 - 50% (mass per mass).

The non-wettability of said LAS-ceramic product is improved according to the invention by incorporating BaSO_4 as non-wetting agent in the product in any
10 one of the following two methods :

1. BaS - Impregnation

- (i) A solution of BaS is prepared by intimately mixing one mass part of BaSO_4 with half a mass part of carbon, and firing the mixture at
15 1190°C for 2 hours;
- (ii) One mass part of the product of step (i) is added to four mass parts water; boiled for 12 hours; and the solids filtered off;
- (iii) The solution resulting from step (ii) is kept at boiling point, and the semi-porous LAS-ceramic product immersed in the boiling
20 solution for 15 minutes;
- (iv) The impregnated product is air-dried and then calcined at 500 - 800°C for 3 hours.

2. BaCl₂ - Impregnation

- 5 (i) A saturated solution of BaCl₂ is prepared by dissolving 59g BaCl₂ in 100ml H₂O at 100°C. (Alternatively 1 kg BaCO₃ in 0,95kg H₂O is treated with 1,11kg HCl (33% concentration by volume) to form a saturated solution of BaCl₂);
- (ii) A diluted solution of H₂SO₄ (concentration not critical, say 50% (volume by volume) is prepared;
- 10 (iii) A cooled down semi-porous as fired LAS-ceramic product is impregnated with the boiling BaCl₂ – solution;
- (iv) The ceramic product is cooled down to cause BaCl₂ to precipitate out in the pores of the ceramic product;
- 15 (v) Any excess water is removed from the ceramic product under vacuum;
- (vi) The ceramic body is impregnated with the diluted H₂SO₄ which
20 reacts with the BaCl₂ to cause BaSO₄ to precipitate inside the pores of the ceramic product;

- (vii) The ceramic product is dried and calcined to 700°C to remove all volatiles.

In both instances an LAS-ceramic product is formed which is substantially non-wettable with molten aluminium.

It will be appreciated that the invention also includes within its scope an LAS-ceramic product of which the non-wettability has been improved by the incorporation therein of BaSO₄ by any one of the aforesaid two methods.

10

Results obtained with a product according to the Invention

The following results were obtained comparing an LAS-ceramic product according to the invention with products conventionally used in the handling of molten aluminium.

15

In compiling these results, the importance to the process of the relevant refractory property is rated from 1 - 10, and then multiplied by the rating (1 - 10) of the specific ceramic material in terms of the property, in order to generate a normalised rank for the different materials in terms of their total performance.

20

1. Competitive products

	Aluminium Titanate	(AT)
	Fused Silica	(FS)
	Cast Iron	(CI)
5	Fibrous Ceramic Board	(CB)
	Ceramic LAS - Product	(LAS)

2. Weighted properties

	Thermal Shock Resistance	(10)
10	Resistance to Wetting	(8)
	Thermal Conductivity/Capacity	(5)
	Strength	(5)

3. Material ratings

15	3.1	<u>Thermal Shock (x 10)</u>		
		AT	10	(100)
		FS	10	(100)
		CI	10	(100)
		CB	6	(60)
20		LAS	10	(100)

3.2 Wettability (x 8)

AT	10	(80)
FS	4	(32)
CI	0	(0)
CB	10	(80)
LAS	10	(80)

3.3 Thermal Conductivity/Capacity (x 5)

AT	3	(15)
FS	8	(40)
CI	0	(0)
CB	10	(50)
LAS	10	(50)

3.4 Strength (x 5)

AT	10	(50)
FS	6	(30)
CI	10	(50)
CB	2	(10)
LAS	10	(50)

Total Ratings

	Aluminium Titanate	(AT)	(245)	=	± 9
	Fused Silica	(FS)	(207)	=	± 7
	Cast Iron	(CI)	(150)	=	± 5
5	Ceramic Board	(CB)	(200)	=	± 7
	Ceramic LAS - product	(LAS)	(280)	=	± 10

It is clear from the above results that when used for the handling of molten aluminium, an LAS-ceramic product according to the invention has much better
10 overall properties than those of the aforementioned known products.

It will also be appreciated that there are no doubt any variations in detail possible with a ceramic product according to the invention without departing from the spirit and/or scope of the claims.

CLAIMS

1. A ceramic product, characterised in that it contains at least 70% lithium aluminium silicate on a mass per mass basis.
- 5 2. The ceramic product of claim 1, characterised in that the lithium aluminium silicate comprises petalite in finely divided form which has been fired to a temperature in the order of between 1150°C and 1210°C.
- 10 3. The ceramic product of claims 1 or 2, characterised in that it comprises substantially 100% lithium aluminium silicate on a mass per mass basis.
- 15 4. The ceramic product of any one of the preceding claims, characterised in that it includes a non-wetting agent which has been incorporated in the fired LAS-ceramic product.
5. The ceramic product of claim 4, characterised in that the non-wetting agent comprises barium sulphate.
- 20 6. A method of improving the non-wettability of the ceramic product of any one of claims 1 to 3, characterised in that it includes the step of providing a non-wetting agent such as barium sulphate in the fired LAS-ceramic product.

7. The method of claim 6, characterised in that the barium sulphate is provided in the fired LAS-ceramic product by impregnating the semi-porous fired LAS-ceramic product with a saturated aqueous solution of barium sulphide (BaS) which, after drying, is oxidised in situ to BaSO₄.
8. The method of claim 7, characterised in that the oxidation is effected by calcining the dried product to 500 - 800°C in an oxidising atmosphere.
9. The method of claim 6, characterised in that the BaSO₄ is provided by impregnating the semi-porous fired LAS-ceramic product with a solution of BaCl₂, and then treating the product with sulphuric acid to cause BaSO₄ to precipitate inside the pores of the ceramic product.
10. The method of claim 9, characterised in that the BaCl₂ - solution is a substantially saturated one, and the sulphuric acid comprises diluted sulphuric acid.
11. A method of forming the ceramic product of any one of claims 1 to 5, characterised in that it includes the step of firing petalite in finely divided form to a temperature in the order of between 1150°C and 1210°C.

12. The method of claim 11, characterised that the product is formed by means of any one of the following methods: slip casting; extrusion or injection moulding; wet or dry pressing.

5 13. The method of any one of claims 11 or 12, characterised in that the finely divided petalite may comprise a mixture of two fractions:

- a first one having an average particle size in the order of 1 micrometer, used in a concentration from 50 to 100% (mass per mass); and
- 10 - a second one having a particle size in the order of 75 micrometer, used in a concentration of from 0 - 50% (mass per mass).

INTERNATIONAL SEARCH REPORT

Inter. Appl. No.
PCT/ZA 99/00095

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C04B35/19 C04B41/85

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 198027 Derwent Publications Ltd., London, GB; Class J04, AN 1980-47258C XP002126183 -& JP 55 067563 A (NGK SPARK PLUG CO LTD), 21 May 1980 (1980-05-21) abstract; table 1	1-3, 11-13
X	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 06, 30 June 1997 (1997-06-30) & JP 09 030860 A (NORITAKE CO LTD), 4 February 1997 (1997-02-04) abstract	1-3, 11-13

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Fax: (+31-70) 340-3016

Authorized officer

Rosenberger, J

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Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 55067563 A	21-05-1980	JP 1298524 C JP 60025386 B	31-01-1986 18-06-1985
JP 09030860 A	04-02-1997	NONE	

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